

CERAMIC PIGMENTS BASED ON RAW MATERIALS FROM UZBEKISTAN

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Green, blue and turquoise ceramic pigments have been obtained by means of heterovalent substitution of atoms based on calcium aluminosilicate (anorthite) with calcium and silicon ions replaced by transition elements and aluminum using quartz sand from the Navoinskoe deposit, Samarkand chalk and alumina-containing wastes from the Shurtanskii Gas-Chemical Complex. The physical-chemical properties of the pigments were studied. The new ceramic pigment compositions were used to produce a commercial test lot of decorative majolica.

Key words: ceramic pigments, aluminosilicates, porcelain, faience, production wastes, reflection spectra, chemical stability.

In the Republic of Uzbekistan three or four state enterprises and about 80 small private workshops are actively producing porcelain housewares and faience based on local as well as imported raw materials and ceramic mixes. These enterprises use ceramic pigments imported mainly from abroad to decorate articles. The quality of the articles produced is noticeably inferior to the foreign analogs, mainly in regards to aesthetic appearance and marketability, assortment, design and other factors.

The quality and assortment of artistically appealing porcelain-faience articles can be improved by using high-quality pigments, which can be obtained on the basis of highly efficient technologies and accessible raw materials.

On this basis, we studied the synthesis of ceramic pigments with a wide range of colors by means of directed synthesis based on iso- and heterovalent substitution of atoms in the structure of anorthite.

Framework aluminosilicates, a class of minerals that includes the calcium feldspar anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$, possess a

number of valuable properties, such as high thermal and chemical stability and microhardness [1]. In this connection they are of practical and scientific interest for use as a matrix when replacing Ca and Si atoms by Al atoms and transition *d*-elements, characterized by an incomplete electron shell with high polarizability.

Reaction materials and natural raw materials and production wastes were used to solve the problems posed above. The chemical compositions of the natural raw material and production wastes used are presented in Table 1.

The pigments were synthesized by means of a reaction in the solid phase at temperature $1250 \pm 25^\circ\text{C}$ with 1 h isothermal soaking at the maximum temperature. The annealing regime of the pigments is shown in Fig. 1.

X-ray phase analysis of the pigment synthesis processes showed that the x-ray diffraction pattern of the green pigment synthesized on the basis of natural raw materials contains diffraction peaks attesting to the presence of the following: corundum (0.345, 0.281, 0.255, 0.237, 0.210, 0.173, 0.159 nm), quartz (0.331, 0.211, 0.197, 0.163 nm), anorthite (0.320, 0.281, 0.249, 0.210, 0.200, 0.176, 0.162 nm) and spinels (0.241, 0.200 nm). According to the intensity of the re-

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TABLE 1. Chemical Composition of Raw Materials

Material	Content, wt. %								
	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	other
Samarkand chalk	1.01	0.24	54.66	19.80	—	—	—	—	44.01
Navoinskoe quartz sand	87.20	5.22	0.56	0.64	0.89	0.58	1.94	0.20	2.77
Alumina-containing waste from the Shurtanskii Gas-Chemical Combine	—	90.22	5.88	—	0.05	3.32	0.08	—	0.45

TABLE 2. Chemical Composition of the Optimal Compositions of the Pigments

Pigment color	Content, wt. %								
	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃ TiO ₂	Na ₂ O K ₂ O	Co ₂ O ₃	Ni ₂ O ₃	Cr ₂ O ₃
Green	29.90	40.35	13.93	0.19	0.26	2.03	–	–	13.35
Turquoise	27.22	44.38	9.93	0.17	0.23	2.09	–	16.08	–
Blue	33.90	36.94	16.32	0.21	0.30	2.05	10.40	–	–

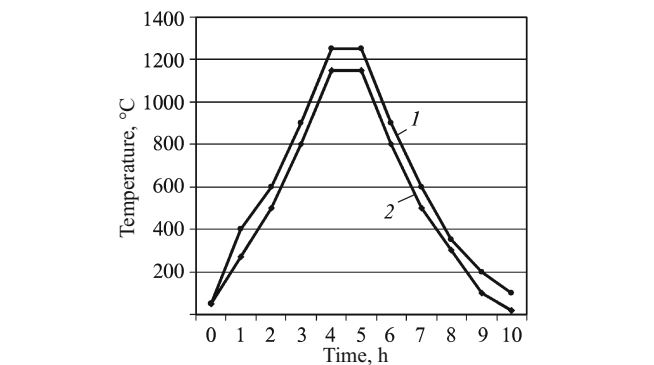


Fig. 1. Annealing regime used for the pigments: 1) chrome- and nickel-containing; 2) cobalt-containing.

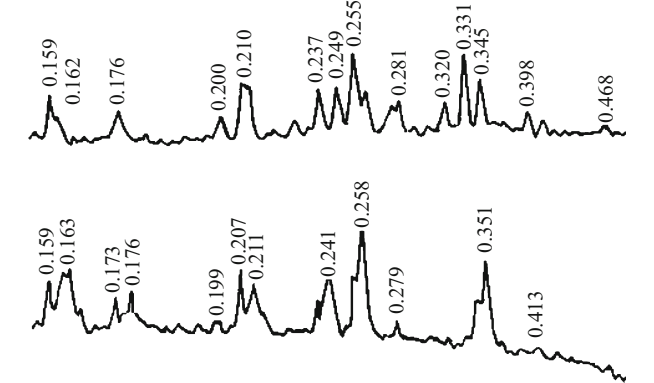


Fig. 2. X-ray diffraction patterns of chromium-containing pigments obtained on the basis of raw materials.

flections the predominant minerals in the product of annealing are corundum and spinel, the quartz reflections are also

TABLE 3. Color Characteristics of Chromium-Containing Pigments

Pigment color	Color coordinates			Chromaticity coordinates		
	x	y	z	X	Y	Z
Green	16.46	18.87	16.07	0.322	0.367	0.313
Blue	7.00	7.18	11.07	0.277	0.284	0.438
Turquoise	18.32	19.90	14.52	0.347	0.377	0.275

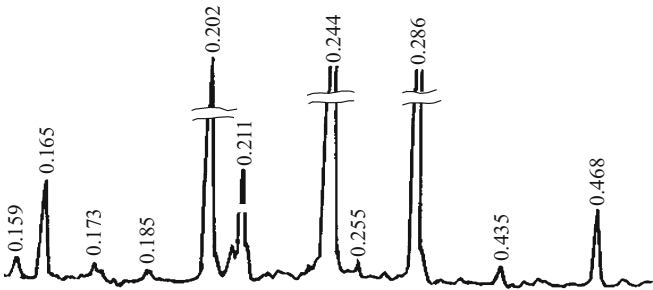


Fig. 3. X-ray diffraction pattern of a cobalt-containing pigment obtained on the basis of natural raw materials.

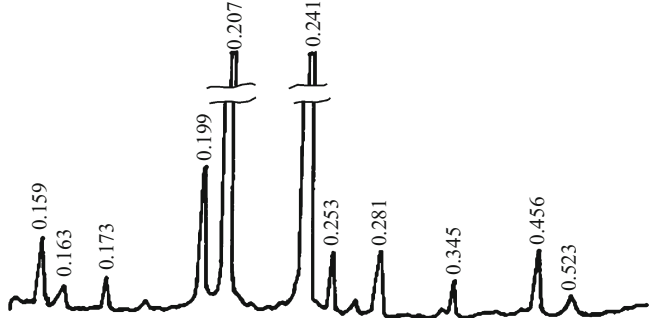


Fig. 4. X-ray diffraction pattern of the turquoise pigment.

clearly visible, and weak anorthite reflections are also present (Fig. 2).

The x-ray diffraction pattern of the blue pigment obtained on the basis of raw materials contains mainly reflections due to spinel (0.468, 0.286, 0.255, 0.244, 0.211, 0.202, 0.165 nm) and corundum (0.345, 0.255, 0.159 nm). The spinel reflections are stronger than the corundum reflections (Fig. 3).

The x-ray diffraction pattern of the turquoise pigment shows reflections due to corundum (0.345, 0.261, 0.253, 0.241, 0.228, 0.207, 0.173, 0.153 nm) and spinels (0.468, 0.281, 0.267, 0.241, 0.200, 0.181, 0.164, 0.162, 0.155 nm). Both the corundum and spinel reflections are quite strong (Fig. 4).

The color characteristics and physical-chemical properties of the ceramic pigments were determined by standard techniques and are presented in Tables 3 and 4.

TABLE 4. Physical-Chemical Properties of the Ceramic Pigments

Property	Compositions		
	Green	Turquoise	Blue
Density, g/cm ³	2.70	2.81	2.84
Thermal stability, °C, higher than	1300	1300	1300
Chemical stability, %:			
1 N NaOH	97.5	98.1	98.7
1 N CH ₃ COOH	95.4	95.8	96.1

In summary, the compositions of green, blue and turquoise ceramic pigments based on calcium aluminosilicate

with the general formula $\text{Ca}_{1-x}\text{Me}_x\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ with calcium replaced by transition elements and silicon by aluminum using quartz sand from the Navoinskoe deposit and Samarkand chalk and alumina-containing wastes from the Shurtanskii Gas-Chemical Combine.

A trial lot of decorative majolica was produced using the new compositions developed for ceramic pigments of different colors and tested under operating conditions at the enterprise.

REFERENCES

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